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(21) International Application Number: PCT/EP99/03453 (22) International Filing Date: 18 May 1999 (18.05.99) (30) Priority Data: 98201681.8 20 May 1998 (20.05.98) EP (71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): GALINA, Claudio [BE/BE]; Avenue Jean Monnet 1, B-1348 Ottignies, Louvain-la-Neuve (BE).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYOL BLEND FOR THE PREPARATION OF OPEN CELL RIGID POLYURETHANE FOAMS (57) Abstract <p>Polyol blend comprising: (a) a polyol component having an average hydroxyl value of 150 to 850 mg KOH/g and (b) a polymer polyol comprising a polymer stably dispersed in a base polyol medium, which base polyol medium has an average primary hydroxyl content of less than 20 %. This polyol blend is suitably applied in a process for the preparation of open cell rigid polyurethane foams, wherein it is reacted with a polyisocyanate component in the presence of at least a catalyst, a foam stabilising agent and a blowing agent. The resulting open cell rigid polyurethane foam has a density of less than 50 kg/m³ and a closed cell content of less than 10 %, preferably of less than 5 % and can suitably be applied as heat insulating material.</p>		

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POLYOL BLEND FOR THE PREPARATION OF OPEN CELL
RIGID POLYURETHANE FOAMS

The present invention relates to a polyol blend for the preparation of open cell rigid polyurethane foams, to a process for preparing open cell rigid polyurethane foams, to the polyurethane foams obtainable by this process and to shaped articles comprising these polyurethane foams.

In general, rigid polyurethane foams are well known for their excellent heat insulating properties. Particularly closed cell polyurethane foams, are widely used as heat insulating material in e.g. pipings, storage tanks, buildings and refrigerators. Closed cell polyurethane foams used to be made with blowing agents based on chlorofluorocarbons (CFC's) of which R-11 (trichlorofluoromethane) was a frequently applied example. The heat insulating properties were for a large part determined by the thermal conductivity of CFC gases, which filled the cells of the foam. However, due to the ozone depleting effect of CFC's their use has become subject to strict environmental regulations and hence is limited nowadays. Alternative blowing agents have been investigated and are actually used, but is very difficult to find substitutes for CFC as a blowing agent, which have equally low thermal conductivity properties.

Although open cell rigid polyurethane foams have not such excellent heat insulating properties as closed cell rigid foams, their thermal conductivity is still sufficient to be useful as a heat insulating material. Furthermore, the dimensional stability at low foam density of open cell foams is better than that of closed-cell foams. Open cell rigid polyurethane foams,

accordingly, are very suitable for application as the core material in vacuum insulation panels. Such panels usually comprise a core material enclosed in a vacuum container of metal and/or plastic films. Furthermore, open cell rigid polyurethane foams can be used in those rigid foam applications, which do not require any heat insulating properties, but which do require some structural support, for instance, use for automotive headliners or packaging.

Several methods have been proposed to prepare open cell rigid polyurethane foams. For instance, in EP-A-0,547,515 a method for preparing open cell rigid polyurethane foams is disclosed, wherein a polymethylene polyphenylisocyanate prepolymer with a polyol at an NCO/OH equivalent ratio of 1.3 to 3.0 using water as the sole blowing agent in the presence of a catalyst, a foam stabiliser and a cell opening agent. The cell opening agent suitably is a divalent metal salt of a fatty acid, such as calcium stearate, magnesium stearate, strontium stearate or calcium myristate.

According to EP-A-0,567,027 open cell rigid polyurethane foams are prepared by using water as a blowing agent in combination with a specific polyol mixture comprising two or three polyols having different hydroxyl values, said mixture having a hydroxyl value of 160-360 mg KOH/g.

Another method is described in EP-A-0,581,191, where an open cell rigid polyurethane foam is prepared by reacting a polyol with a prepolymer obtained by reacting polymethylene polyphenyl polyisocyanate with a monohydric alcohol using a CFC-substitute as blowing agent in the presence of a catalyst, a foam stabiliser and a cell opening agent. The cell opening agent suitably is a divalent metal salt of a fatty acid, such as calcium stearate.

In G. Burkhart and H. Schator, 35th Annual Polyurethane Technical/Marketing Conference, October 9-12, 1994, pp. 311-315 a method for producing open cell rigid polyurethane foams is disclosed, wherein the open cell structure is achieved by using a specific anti-foaming agent (viz. Tegostab 8919; Tegostab is a trademark) in combination with an appropriate silicone surfactant.

Although these methods are effective in producing open cell rigid polyurethane foams, there is still room for improvement. It would be beneficial if open cell rigid polyurethane foams could be provided having a very low density in combination with good mechanical or structural stability, as such low density foams are attractive for use in a wide variety of applications including the application as heat insulating material. The low density is especially desired, because the low weight of the foam facilitates transportation and handling of e.g. insulation panels. Moreover, a lower density also means that less starting material is necessary to prepare the same volume of foam as compared to the situation in which a higher density foam is to be prepared. Clearly this is advantageous from an economic perspective. Furthermore, it would be attractive if low density open cell rigid foams could be prepared without needing any cell-opener or anti-foaming agent, thus facilitating the manufacture whilst still obtaining excellent foams.

Accordingly, the present invention relates to a polyol blend comprising:

- (a) a polyol component having an average hydroxyl value of 150 to 850 mg KOH/g and
- (b) a polymer polyol comprising a polymer stably

dispersed in a base polyol medium, which base polyol medium has an average primary hydroxyl content of less than 20%.

5 Essentially, the present invention combines a rigid polyol component (component (a)) with a particular polymer polyol (component (b)), which is normally used in the manufacture of flexible polyurethane foams. This specific combination of polyols has been found to result in open cell rigid foams having excellent properties without the need to apply cell-opening agents or anti-foaming agents.

10 The quantities in which the polyol and the polymer polyol are used may vary within broad limits, but preferably the polyol blend according to the present invention comprises 2 to 25 parts by weight, more preferably 2 to 10 parts by weight, of polymer polyol (b) per 100 parts by weight of polyol component (a). The polyol component (a) can be any rigid polyol or combination of rigid polyols having an average hydroxyl value of 150 to 850 mg KOH/g. Such rigid polyols are known in the art. Commonly applied rigid polyols, which can be suitably applied in the polyol blend of the present invention, are polyoxyalkylene polyols have a nominal molecular weight of from 300 to 1500, suitably 500 to 1000, and a nominal average functionality of at least 2.0, suitably from 2.5 to 6. For the purpose of the present invention the average hydroxyl number preferably has a value in the range of from 150 to 650 mg KOH/g. The polyol component (a) may comprise a single rigid polyol, but may also comprise two or more rigid polyols. In a preferred embodiment the polyol component (a) comprises a polyol having a hydroxyl value of 150 to 400 mg KOH/g and a polyol having a hydroxyl value of 400 to 650 mg KOH/g. An example of a rigid polyol having a lower hydroxyl value is CARADOL GB250-01, while examples of rigid

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polyols having a higher hydroxyl value are CARADOL LP530-03 and CARADOL LP585-01 (CARADOL is a trademark).

5 The polymer polyol used as component (b) may in principle be any polymer polyol comprising a polymer stably dispersed in a base polyol medium, provided the base polyol medium has an average primary hydroxyl content of less than 20% based on the total of hydroxyl groups present on the polyol(s) forming the base polyol medium. Accordingly, the base polyol medium may consist of one or more polyols provided the average primary hydroxyl content of these polyol(s) is less than 20%, preferably less than 10% and most preferably less than 5%. The polymer polyol component (b) suitably comprises 15 such a base polyol medium and a polymer stably dispersed therein in an amount of 5 to 40% by weight based on total weight of polymer polyol. In a further preferred embodiment the base polyol medium consists of a polyoxyalkylene polyol having a molecular weight in the 20 range of from 250 to 12,000, preferably from 500 to 6,500, more preferably from 2,500 to 6,000; an average nominal functionality (F_n) of at least 2.0, more preferably from 2.5 to 6.0 and most preferably from 2.5 to 3.5; and a primary hydroxyl content of at most 10%, 25 more preferably at most 5%. Since the base polyol medium most preferably has a very low average primary hydroxyl content, very good base polyols are those having a very low ethylene oxide (EO) content resulting from EO tipping. Suitably, the ethylene oxide content resulting from ethylene oxide tipping is less than 1% by weight, 30 while most suitably the polyol has not been tipped with EO at all.

The polymer, which is stably dispersed in the base polyol medium, may in principle be any such polymer known 35 to be applicable for this purpose. Thus, suitable

polymers include the polymers based on ethylenically unsaturated monomers and particularly polymers of vinyl aromatic hydrocarbons, like styrene, alpha-methyl styrene, methyl styrene and various other alkyl-substituted styrenes. Of these, the use of styrene is preferred. The vinyl aromatic monomer may be used alone or in combination with other ethylenically unsaturated monomers, such as acrylonitrile, methacrylonitrile, vinylidene chloride, various acrylates and conjugated dienes like 1,3-butadiene and isoprene. Preferred polymers, however, are polystyrene and styrene-acrylonitrile (SAN) copolymers. Another suitable class of polymers are the polyurea and polyurethane polymers. Particularly the condensation products of polyhydric alcohol amines and aromatic diisocyanates are very useful in this respect. A very much preferred polymer is the condensation product of triethanol amine and toluene diisocyanate (TDI). For the purpose of the present invention it is preferred that the dispersed polymer is polystyrene, SAN copolymer, polyurea or the polyurethane polymer obtained as the condensation product of triethanolamine and toluene diisocyanate.

The dispersed polymer is suitably present in an amount of from 5 to 40% by weight based on total weight of polymer polyol. In case the polymer is polystyrene or SAN polymer, preferred amounts are between 5 and 35% by weight, whilst in case of polyurea polyurethane polymers the preferred amount of polymer is between 5 and 20% by weight.

The polyol blend according to the present invention is very suitable for the preparation of open cell rigid polyurethane foams. Thus, the present invention also relates to a process for the preparation of open cell rigid polyurethane foams, which process comprises reacting the polyol blend described herein before with a

polyisocyanate component in the presence of at least a catalyst, a foam stabilising agent and a blowing agent.

Polyisocyanates that may be used are those conventionally applied in the production of rigid polyurethane foams. Useful polyisocyanates should contain at least two isocyanate groups and include both aliphatic -usually alkylene- and aromatic di-, tri-, tetra- and higher isocyanates known in the art to be suitably applied in the production of rigid polyurethane foams.

Mixtures of two or more of such aliphatic and/or aromatic polyisocyanates may also be applied. Examples of suitable polyisocyanates, then, include 2,4-toluene diisocyanate (2,4-TDI), 2,6-TDI, mixtures of 2,4-TDI and 2,6-TDI, 1,5-naphthene diisocyanate, 2,4-methoxyphenyl diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate and 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4',4"-triphenylmethane triisocyanate, 2,4,6-toluene triisocyanate, 4,4'-dimethyl-2,2', 5,5'-diphenylmethane tetraisocyanate, polymethylene-polyphenylene polyisocyanate and mixtures of two or more of these. Polymeric MDI, a mixture of polyisocyanates with MDI as the main component, may also be used. For the purpose of the present invention it has been found particularly advantageous to use polymeric MDI.

The quantity of polyisocyanate component to be used should suitably be such that the isocyanate index has a value between 50 and 150, most suitably between 80 and 130. However, isocyanate indices outside these ranges may also be used.

Catalysts for the production of rigid polyurethane foams are known in the art and include many different compounds. For the purpose of the present invention suitable catalysts include tertiary amines, such as, for

instance, bis(2,2'-dimethylamino)ethyl ether,
trimethylamine, triethylamine, triethylenediamine and
dimethylethanolamine (DMEA). Tin-based catalysts may also
be applied and include tin salts and dialkyl tin salts of
5 carboxylic acids. Specific examples are dibutyltin
dilaureate, stannous octoate, stannous oleate, dibutyltin
acetate and dibutyltin diacetate. Also trimerisation
catalysts like potassium acetate may be applied. The
catalyst is typically used in an amount of from 0.01 to
10 7 php (parts by weight per 100 parts of polyol).

The foam stabiliser (or surfactant) used in the
present process may be any polyurethane foam stabiliser
useful in the production of rigid polyurethane foams.
Organosilicone or organopolysiloxane surfactants are most
15 conventionally applied as foam stabilisers in
polyurethane production. A large variety of such
surfactants is commercially available. Usually, such foam
stabiliser is used in an amount of up to 3 php.

A blowing agent is also present in the process
20 according to the present invention. Suitable blowing
agents include water, acetone, (liquid) carbon dioxide,
halogenated hydrocarbons, aliphatic alkanes, such as n-
pentane and isopentane, and alicyclic alkanes, such as
cyclopentane and cyclohexane. It will be understood that
25 these blowing agents may be used singly or in mixtures of
two or more. For the purpose of the present invention, it
has been found particularly advantageous to use water as
the sole blowing agent. The amount in which the water is
used may vary between wide limits, but very good results
30 have been achieved when using water in an amount of
2-12 php.

In addition, other well known auxiliaries, such as
flame retardants, antioxidants, colouring agents and
fillers may also be used.

In a further aspect the present invention relates to an open cell rigid polyurethane foam obtainable by the process described herein before, which polyurethane foam has a density of less than 50 kg/m^3 and a closed cell content of less than 10%, preferably of less than 5%. Preferred foams, which are obtainable by the present process, have densities of 10 to 30 kg/m^3 , more preferably 10 to 25 kg/m^3 .

The present invention also relates to shaped articles comprising the open cell rigid polyurethane foam defined in the preceding paragraph as well as to heat insulating materials comprising this open celled rigid polyurethane foam in a laminate structure.

The invention is further illustrated by the following examples, but is by no means limited to the specific embodiments demonstrated therein.

The components used in the examples are:

Polyol components

Polyol A: A rigid, aromatic, amine-group containing, propylene oxide(PO)-based polyether polyol having a hydroxyl value of 530 mg KOH/g.

Polyol B: A rigid, glycerol initiated polyether polyol having a hydroxyl value of 250 mg KOH/g.

PP-A: A polymer polyol containing (i) a base polyol being a EO/PO based, glycerol initiated polyether polyol having a primary hydroxyl content of essentially 0%, a molecular weight of 3500 and a hydroxyl value of 37 mg KOH/g and (ii) stably dispersed therein 20 wt% polystyrene.

PP-B: A polymer polyol containing (i) the same base polyol as PP-A, and (ii) stably dispersed therein 40 wt% styrene-acrylonitrile copolymer.

PP-C: A polymer polyol containing (i) a base polyol being a EO/PO based, glycerol initiated polyether polyol having a primary hydroxyl content of 80%, a molecular weight of 4700 and a hydroxyl value of 25 mg KOH/g and containing 14 wt% EO-tip and (ii) stably dispersed therein 28 wt% polystyrene.

PP-D: A polymer polyol containing (i) the same base polyol as PP-C, and (ii) stably dispersed therein 15 wt% styrene-acrylonitrile copolymer.

Ancillary chemicals

DMEA : Dimethylethanolamine
AM58 : trimerisation catalyst ex Resina Chemie
TCPP : tris(chloropropyl)phosphate (flame retardant)
B8404 : Tegostab B8404 (silicone surfactant) ex Goldschmidt

Isocyanate

MDI : polymeric diphenylmethane diisocyanate

Example 1

A polyol formulation was prepared consisting of 30 parts by weight (pbw) Polyol A, 70 pbw Polyol B and 10 pbw of PP-A. Subsequently a foaming formulation (Ex-1) was prepared having a composition as indicated in Table I.

The formulation was allowed to foam in a bag. After foaming a sample of the foam was taken and density and closed cell content were determined.

Example 2

Example 1 was repeated except that 10 pbw of PP-B were added (Ex-2) in stead of PP-A.

The composition of the foaming formulation and the properties of the resulting foam are indicated in Table I.

Comparative Examples 1 and 2

Example 1 was repeated except that 10 pbw of PP-C (CEx-1) or 10 pbw of PP-D (CEx-2) were used in stead of 10 pbw of PP-A.

5 The composition of the foaming formulations and the properties of the resulting foam are indicated in Table I.

TABLE I Foaming formulations

	Ex-1	Ex-2	CEx-1	CEx-2
Polyol A (pbw)	70	70	70	70
Polyol B (pbw)	30	30	30	30
PP-A (pbw)	10	-	-	-
PP-B (pbw)	-	10	-	-
PP-C (pbw)	-	-	10	-
PP-D (pbw)	-	-	-	10
DMEA (pbw)	2.4	2.4	2.4	2.4
AM58 (pbw)	1.6	1.6	1.6	1.6
B8404 (pbw)	2.0	2.0	2.0	2.0
water (pbw)	10.2	10.2	10.2	10.2
TCPP (pbw)	10	10	10	10
MDI (pbw)	208	208	208	208
Isocyanate index	90	90	90	90
Density (kg/m3)	16.8	16.6	17.52	17.5
Closed cell content (%)	2	3	42	60

From Table I it can be seen that the polyol formulation according to the present invention result in foams having a slightly lower density and a much lower closed cell content.

Example 3

10 A laminate with a open cell polyurethane foam prepared with a polyol blend according to the present invention, was made on a continuous laminator machine.

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The laminator machine is a high pressure, multi-component unit, manufactured by Cannon/Viking UK. The urethane system, being a blend of four different streams, was dispensed on the bottom facing through a perforated pipe, fitted to a traversing mixing head. As the facing, polyethylene coated kraft paper was used. The machine output was adjusted to produce 60 mm thick, 600 mm wide laminates at an overall target density of 22 kg/m³ at a belt speed of 2.9 m/min. The 6 meter conveyor section was working in free rise mode.

As stated above, four streams (denoted as "polyol blend", "cat 1 blend", "cat 2 blend" and "MDI") are pumped into the mixing head, where they are thoroughly mixed and dispensed onto the facing. The MDI stream consisted of polymeric MDI. The compositions of the other three streams are indicated in Table II. The amounts are indicated in parts by weight (pbw).

TABLE II Feed stream compositions

	polyol blend	cat 1 blend	cat 2 blend
Polyol A	30	-	-
Polyol B	56.2	15	10
PP-A	10	-	-
TCPP	10	-	-
B8404	2	-	-
DMEA	-	-	6
AM58	-	-	4
water	-	15	-

The stream rates were:

Output polyol blend : 0.84 l/min
Output MDI : 1.08 l/min
Output cat 1 blend : 0.136 l/min
Output cat 2 blend : 0.033 l/min

The temperature of both polyol blend and MDI stream was 19 °C, the temperature of the belt was kept at 35 °C.

The properties of the open cell rigid foam-based laminate were:

5	Density	:	22 kg/m ³
	Closed cell content	:	2%
	Compressive strength		
	in rise direction	:	80 kPa
	in production direction	:	55 kPa
10	in side direction	:	55 kPa
	Dimensional stability at 70 °C at 95% relative humidity after 24 hours		
	in rise direction	:	3.5%
	in production direction	:	-0.5%
15	in side direction	:	-0.7%
	Thermal conductivity at 10 °C	:	35 mW/(m.K)

Thermal conductivity at 10 °C was determined by putting the laminate between two plates, one having a temperature of 0 °C and the other having a temperature of 20 °C, and determining the amount of heat transferred through the laminate from the warm plate to the cold plate per second per meter of laminate per degree Kelvin temperature difference.

From these data it can be seen that the laminate has a relatively low density and a low closed cell content, while at the same time exhibiting excellent mechanical stability and low thermal conductivity, thus making it very useful as an insulating material.

C L A I M S

1. Polyol blend comprising:
 - (a) a polyol component having an average hydroxyl value of 150 to 850 mg KOH/g and
 - (b) a polymer polyol comprising a polymer stably dispersed in a base polyol medium, which base polyol medium has an average primary hydroxyl content of less than 20%.
2. Polyol blend according to claim 1, comprising 2 to 25 parts by weight of polymer polyol (b) per 100 parts by weight of polyol component (a)
3. Polyol blend according to claim 1 or 2, wherein the polyol component (a) comprises a polyol having a hydroxyl value of 150 to 400 mg KOH/g and a polyol having a hydroxyl value of 400 to 650 mg KOH/g.
4. Polyol blend according to any one of the preceding claims, wherein the polymer polyol (b) comprises a base polyol medium having an average primary hydroxyl content of at most 10% and a polymer stably dispersed therein in an amount of 5 to 40% by weight based on total weight of polymer polyol.
5. Polyol blend according to claim 4, wherein the base polyol medium has an average primary hydroxyl content of at most 5%.
6. Polyol blend according to any one of the preceding claims, wherein the polymer polyol (b) comprises a base polyol medium consisting of a polyoxyalkylene polyol having a molecular weight in the range of from 250 to 12,000, an average nominal functionality (F_n) of at least 2.0 and a primary hydroxyl content of at most 10% and a polymer stably dispersed therein in an amount of 5 to 40% by weight based on total weight of polymer polyol.

7. Polyol blend according to claim 6, wherein the polyoxyalkylene polyol has a molecular weight in the range of from 2,500 to 6,000, a \bar{P}_n in the range of from 2.5 to 3.5 and a primary hydroxyl content of at most 5%.

5 8. Polyol blend according to claim 6 or 7, wherein the polyoxyalkylene polyol has an ethylene oxide content resulting from ethylene oxide tipping of less than 1% by weight.

9. Polyol component according to any one of claims 4 to 10 8, wherein the stably dispersed polymer is polystyrene, SAN copolymer, polyurea or the polyurethane polymer obtained as the condensation product of triethanolamine and toluene diisocyanate.

10. Process for the preparation of open cell rigid 15 polyurethane foams, which process comprises reacting a polyol blend as claimed in any one of claims 1-9 with a polyisocyanate component in the presence of at least a catalyst, a foam stabilising agent and a blowing agent.

11. Process according to claim 10, wherein the 20 polyisocyanate component comprises polymeric MDI.

12. Process according to claim 10 or 11, wherein the blowing agent is water.

13. Process according to claim 12, wherein water is present in an amount of 5-12 parts by weight per 25 100 parts by weight of polyol component (a).

14. An open cell rigid polyurethane foam obtainable by the process according to any one of claims 10-13, which polyurethane foam has a density of less than 50 kg/m³ and a closed cell content of less than 10%, preferably of 30 less than 5%.

15. Open cell rigid polyurethane foam according to claim 14 having a density of 10 to 30 kg/m³.

16. Shaped article comprising the open cell rigid polyurethane foam according to claim 14 or 15.

17. A heat insulating material comprising the open celled rigid polyurethane foam according to claim 14 or 15 in a laminate structure.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/63 C08G18/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 248 704 A (ROSSIO RICHARD C ET AL) 28 September 1993 (1993-09-28) column 1, line 56 - column 6, line 59 examples 2,3; table 1	1,4-6, 8-14,16
X	US 4 866 102 A (PRAY EDWARD R ET AL) 12 September 1989 (1989-09-12) column 1, line 24 - column 9, line 15 example 45	1,6-9, 14,16
A	US 5 698 609 A (LOCKWOOD ROBERT JOHN ET AL) 16 December 1997 (1997-12-16) column 2, line 13 - column 7, line 5 example 3; table 2	1,9-12, 14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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